

Structure of Modulated Molecular Crystals. VI. Lattice-Energy Analysis of the Modulated Phase of Thiourea

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Abstract

The lattice energy of the one-dimensionally modulated intermediate-temperature phase of thiourea has been calculated by direct numerical integration over the modulation coordinate, using a new modification of the program *WMIN*. Two different descriptions are used for the N–H...S interactions. The first, a purely electrostatic model, gives an energy for the modulated phase which is higher than that of either the paraelectric high-temperature, or the ferroelectric low-temperature phase. The introduction of a Lippincott–Schroeder hydrogen-bonding potential is necessary to account for the lowering of the energy on cooling through the two phase transitions. The results indicate that the modulation is driven by the hydrogen-bonding network in the crystal.

Introduction

Thiourea (CN₂H₄S) undergoes several phase transitions on cooling (Denoyer & Currat, 1986). Between 202 and 169 K, an incommensurately modulated phase occurs with a wavevector $\mathbf{q} = \delta\mathbf{b}^*$, where δ varies with temperature from 1/9 to 1/7.

In order to gain understanding of the occurrence of the modulation, we have redetermined the modulated structure using a rigid-molecule displacement model, which greatly reduces the number of parameters to be determined (Gao, Gajhede, Mallinson, Petricek & Coppens, 1988; Petricek, Coppens & Becker, 1985). The four-dimensional symmetry of the modulated phase $P:P2_1ma:-1-11$ was found to be lower than predicted by Landau theory for a $Pnma$ high-temperature phase. The major molecular displacements are a rotation around the \mathbf{b} axis and a displacement in the $\mathbf{a}-\mathbf{c}$ plane. These are also the main differences between the high-temperature paraelectric and the low-temperature ferroelectric phases. The amplitudes of the displacements increase on cooling in the stability range of the modulation, and seem to approach the displacements occurring in the ferroelectric phase close to the lower boundary of the stability range, indicating that the modulated phase can be considered as a gradual transition from the paraelectric to the ferroelectric structure.

To gain insight into the mechanism of the modulation, we have calculated the lattice energies of all three phases using the pairwise interaction approximation. Our method uses the four-dimensional symmetry description of modulated structures (de Wolff, Janssen & Janner, 1981), according to which all geometries occurring in the crystal are found along one period of the fourth-dimension coordinate t . We have modified the program *WMIN* (Busing, 1981) to allow a general treatment of one-dimensionally modulated structures.

Spectroscopic experiments (Takahashi, Schrader, Meier & Gottlieb, 1967; Bleckmann, Schrader, Meier & Takahashi, 1971), as well as the crystal structures indicate the existence of an N–H...S hydrogen-bonding network in the thiourea crystals. Its contribution to the lattice energy has been treated according to two models, the second of which includes a specific potential function for hydrogen bonding.

Thiourea structures

The crystal structures of paraelectric and ferroelectric phases have been determined by X-ray and neutron diffraction (Truter, 1967; Goldsmith & White, 1959; Elcombe & Taylor, 1968). The crystallographic data are listed in Table 1, together with those of the modulated phase. The atomic coordinates from the neutron study (Elcombe & Taylor, 1968) and the coordinates and displacement amplitudes of the modulated phase are listed in Tables 2(a) and 2(b) respectively. The H-atom positions in the modulated phase were obtained by extending the experimental N–H bond lengths to 1.01 Å, the average of the ferroelectric phase neutron results.

Fig. 1 shows the packing diagrams of the para- and ferroelectric phases. The molecular plane is perpendicular to the mirror planes of the space groups $Pnma$ and $P2_1ma$ respectively, with the C and S atoms located in the mirror planes. In the crystals of the intermediate phase, stable below 202 K, the two independent molecules have somewhat different modulations. The crystals belong to the superspace group $P:P2_1ma:-1-11$. The longitudinal b -axis modulation wave represents a slight displacement of the molecules from the mirror planes occupied in the high- and low-temperature phases.

Table 1. *Space group and cell constants (Å) for the thiourea phases*

Phase	Space group	<i>a</i>	<i>b</i>	<i>c</i>
Paraelectric*	<i>Pnma</i>	7.655	8.537	5.520
Modulated	<i>P: P2₁ma: -1-11</i>	7.540	8.528	5.459
Ferroelectric†	<i>P2₁ma</i>	7.516	8.519	5.494

* Truter (1967).

† Goldsmith & White (1959).

Table 2. *Fractional coordinates and displacement amplitudes*

(a) Fractional coordinates of conventional phases*

	<i>x</i>	<i>y</i>	<i>z</i>
Paraelectric phase			
S	-0.0073	0.2500	0.1148
C	0.0906	0.2500	-0.1635
N(1)	0.1307	0.3829	-0.2773
H(11)	0.1842	0.3761	-0.4405
H(12)	0.0955	0.4870	-0.2054
Ferroelectric phase			
S	0.0062	0.2500	0.0954
C	0.0733	0.2500	-0.2045
N(1)	0.1000	0.3837	-0.3256
H(11)	0.1365	0.3805	-0.5006
H(12)	0.0772	0.4878	-0.2448
S'	0.0272	-0.2500	-0.1285
C'	-0.0985	-0.2500	0.1360
N(1')	-0.1475	-0.3844	0.2412
H(11')	-0.2169	-0.3802	0.4006
H(12')	-0.1028	-0.4886	0.1771

(b) Average structure and modulation amplitudes†

	<i>x</i>	<i>y</i>	<i>z</i>
S	-0.0071	0.2500	0.1154
C	0.0892	0.2500	-0.1661
N(1)	0.1285	0.3830	-0.2793
H(11)	0.1796	0.3728	-0.4494
H(12)	0.0952	0.4874	-0.2047

	Translations (Å)			Rotations (°)		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
Molecule I						
First harmonic	-0.128	0.029	0.103	0.20	-6.21	0.36
Second harmonic	-0.009	-0.009	0.015	-0.25	-0.38	0.77
Molecule II						
First harmonic	-0.112	0.002	0.119	0.92	4.70	0.22
Second harmonic	-0.019	0.009	0.006	0.25	0.18	0.51

* Elcombe & Taylor (1968).

† Gao, Gajhede, Mallinson, Petricek & Coppens (1988).

The types of hydrogen bonds in the network are indicated in Fig. 1. In the noncentrosymmetric phase two center-of-symmetry-related hydrogen bonds are no longer equivalent, leading to six, rather than three, different hydrogen bonds.

Computational method: integration over the modulation parameter *t*

In the atom-atom potential model, the lattice energy is expressed as the sum of pairwise Coulombic, 6-12 Lennard-Jones-type and hydrogen-bonding contributions:

$$W_{\text{lat}} = (1/2Z) \sum_i \sum_{j \neq i} (q_i q_j / r_{ij} - A_i A_j / r_{ij}^6 + B_i B_j / r_{ij}^{12}) + W_{\text{HB}} \quad (1)$$

Here *Z* is the number of formula units per asymmetric unit, the *q*'s represent the atomic charges, *A* and *B* are the Lennard-Jones nonbonded coefficients and *r_{ij}* is the distance between atoms *i* and *j*. The index *i* is over one unit cell and *j* over the whole crystal. The hydrogen-bonding energy *W_{HB}* will be discussed later. Convergence of the long-range Coulombic contributions is achieved by the Ewald-Bertaut-Williams method implemented in the program *WMIN*, which includes a combined summation over direct and reciprocal space (Bertaut, 1952; Williams, 1971).

Since the interatomic distances *r_{ij}* vary from unit cell to unit cell in the incommensurately modulated crystal, an additional integration becomes necessary. In the four-dimensional symmetry description this integration is over the variable *t* in the fourth dimension, which has a periodicity of one. An integration from *t* = 0 to *t* = 1 includes all distances *r_{ij}* existing in the modulated three-dimensional crystal. The position of an atom *i* in the unit cell *n* in three-dimensional space *R*³ is given by:

$$\mathbf{r}_{ni} = \mathbf{r}_i^0 + \mathbf{n} + \sum_l \{ \mathbf{U}_l \sin[2\pi \mathbf{q}_l \cdot (\mathbf{g}_l + \mathbf{n}) - \varphi_l] \} \quad (2a)$$

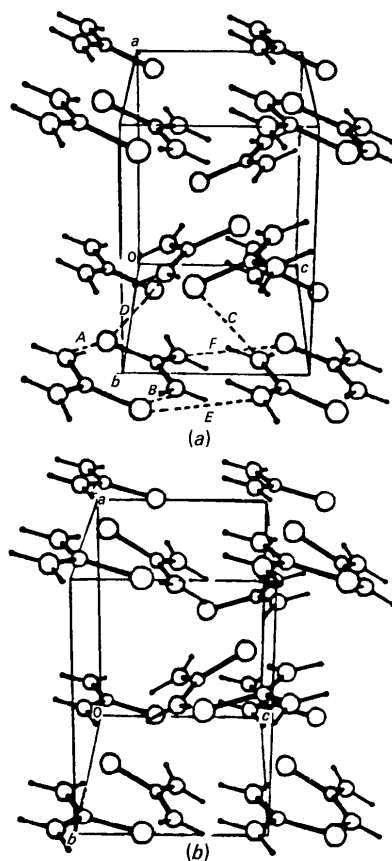


Fig. 1. (a) The structure of the paraelectric phase. The hydrogen bonds, *A, B, C, D* and *E, F*, are pairwise equivalent in the paraelectric phase, but differ in the low-temperature ferroelectric phase. (b) The structure of the ferroelectric phase. In order of descending size, circles represent S, N, C and H atoms.

where l is the order of the harmonic, \mathbf{U}_l is the modulation amplitude vector, \mathbf{q} the wavevector of the modulation, \mathbf{g}_i the phase reference point for the molecule to which atom i belongs and φ_i the phase of the l th harmonic. In four-dimensional space, each atom position is a string in the direction of the basis vector \mathbf{e} perpendicular to $R3$ (de Wolff, 1974). For a unit cell defined by $\mathbf{n} = 0$, the atom position is described by:

$$\mathbf{r}_i(x_1, x_2, x_3, t) = \mathbf{r}_i(x_1, x_2, x_3, 0) + \sum_l \mathbf{U}_l (u_1, u_2, u_3, 0) \times \sin[2\pi(l\mathbf{q}\cdot\mathbf{g}_i + t) - \varphi_i] \quad (2b)$$

where t is the distance from $R3$ in the fourth dimension. The positions of symmetry-related atoms are obtained by application of the symmetry operation:

$$\mathbf{r}' = \mathbf{R}\mathbf{r} + \mathbf{s}$$

and

$$t' = \varepsilon t + \delta - \mathbf{q}\cdot\mathbf{s} \quad (3)$$

where \mathbf{R} and ε are the rotational and \mathbf{s} and δ the translational components of the symmetry element.

Thus $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is a periodic function of t , and a numerical method may be used to integrate the pairwise interactions from $t = 0$ to $t = 1$. With the extended Simpson rule (Press, Flannery, Teukolsky & Vetterling, 1986), the average interaction energy W_{ave} is obtained as:

$$\begin{aligned} W_{\text{ave}} &= \int_0^1 f(t) dt \\ &= (1/N)[1/3f(0) + 4/3f(1/N) + 2/3f(2/N) \\ &\quad + 4/3f(3/N) + \dots + 2/3f(N-2/N) \\ &\quad + 4/3f(N-1/N) + 1/3f(1)] + \mathcal{A}(1/N^4). \end{aligned} \quad (4)$$

N is the number of intervals between $t = 0$ and $t = 1$ and the error \mathcal{A} is of the order $1/N^4$. This expression is applied separately to each of the types of pairwise interactions. The integration error is estimated from the convergence of the series with increasing N . In our work, the results of two calculations with $N/2$ and N intervals was smaller than $0.00001 \text{ kcal mol}^{-1}$ ($1 \text{ kcal mol}^{-1} = 4.1868 \text{ kJ mol}^{-1}$) with N values which never exceeded 1024.

For the reciprocal space summation both main and satellite reflections are to be included. The lattice energy 'structure factor' is a function of reciprocal space vector $\mathbf{Q} = \mathbf{H} + m\mathbf{q}$ (where \mathbf{H} refers to 'main' and $m\mathbf{q}$ to m th-order 'satellite'), and, in analogy with the X-ray case (Petricek, Coppens & Becker, 1985), is expressed as:

$$\begin{aligned} F_p(\mathbf{Q}) &= \sum_i p_i \sum_s \exp\{2\pi i[\mathbf{Q}\cdot\mathbf{r}_i^s - m\varepsilon_s\mathbf{q}\cdot\mathbf{g}_i + m(\delta_s - \mathbf{q}\cdot\mathbf{s}_s)]\} \\ &\quad \times \sum_{m_1, m_2, \dots, m_l = -4}^4 \prod_{k=1}^l J_{-m_k} \{2\pi U^s(k) \\ &\quad \times \exp[-im_k \chi^s(k)]\}, \end{aligned} \quad (5)$$

in which the summation subscripts are restricted by the

expression $m = m_1 + 2m_2 + \dots + lm_l$. In expression (5) the p_i are either the net atomic charges (Coulomb energy) or dispersion coefficients (dispersion energy). The summations over i and s are over the number of atoms in the asymmetric unit and the number of symmetry operations respectively. \mathbf{g}_i is the phase reference point of the rigidly displaced molecule to which atom i belongs, which is usually taken to be the center of mass. U^s and χ^s are the modulation magnitude and phase and J_n is a Bessel function of order n . The index l represents the order of harmonic displacement wave (less than five in our program, not larger than two in the case of thiourea). m values are unlimited; however, in thiourea only values up to $m = 2$ gave significant contributions.

Force-field and hydrogen-bonding models

The atomic charges used in this study were obtained by Crowder, Alldredge & White (1985) from a fit to the *ab-initio* electrostatic potential. They are optimized to reproduce the potential outside the molecular volume. Their values and those of the 6–12 Lennard–Jones coefficients used in this study are listed in Table 3. For the N, C and H atoms the latter are as obtained by Hagler, Huler & Lifson (1974) in a lattice-energy study of nine amide crystals, including urea. The 6–12 nonbonded coefficients of sulfur were obtained by least-squares refinement to fit the experimental lattice energy and the structural parameters of the low-temperature ferroelectric phase. The oxygen 6–12 coefficients were used as starting parameters in this refinement.

A value of $106.6 \text{ kJ mol}^{-1}$ for the enthalpy of thiourea was obtained from vapor pressure measurements at 384 K by de Witt, van Miltenburg & Dekruif (1983). Using experimental values for $c_p(\text{gas})$ and $c_p(\text{solid})$ they derived a value of $-107.8 \text{ kJ mol}^{-1}$ ($-25.76 \text{ kcal mol}^{-1}$) for the enthalpy at 293 K, from which the lattice energy can be obtained with the equation:

$$W_{\text{exp}} = H + 2RT \quad (6)$$

where H is the experimental enthalpy, R the gas constant, and T the absolute temperature.

This room-temperature lattice energy was used in our calculations. Though an error is introduced by not using the true lattice energy for the ferroelectric phase, test calculations showed our results not to be sensitive to small variations in W_{lat} .

The fact that reasonable calculated lattice energies and energy minima can be obtained without accounting for hydrogen bonding (Hagler, Huler & Lifson, 1974; Dove & Lynden-Bell, 1986) might be an indication of the dominance of the electrostatic contributions. However, in several other studies hydrogen bonding has been represented by specific adjustable functions (Derissen & Smit, 1977, 1978; Scott & Scheraga, 1966).

Table 3. Atomic charges and 6–12 nonbonded coefficients used in the calculations

Atomic charges are from Crowder, Alldredge & White (1985) and 6–12 nonbonded coefficients from Hagler, Huler & Lifson (1974); 1 kcal = 4.1868 kJ.

	q (e)	A (kcal Å ³ mol ⁻¹)	B (kcal Å ⁶ mol ⁻¹)
S (model A)*	-0.400	75.88	2868
(model B)*	-0.400	25.83	1569
C	0.166	36.41	1723
N	-0.547	35.08	1506
H(1)	0.349	0.00	0
H(2)	0.316	0.00	0

* Refined values of A and B . Parameters for the other atoms are the same in both models.

In the present study we adopted two models for the hydrogen bonding. The nonbonded coefficients of sulfur were refined for each of the models. In model A , the hydrogen bonds were considered as an electrostatic interaction, following the work of Hagler, Huler & Lifson (1974), in which dispersive and repulsive interactions involving the H atom were omitted. This empirical treatment was recently applied successfully, in a slightly modified form (in which only proton-acceptor interactions were omitted), by Spackman (1986) and Spackman, Weber & Craven (1988). In model B , the hydrogen-bond potential was specifically introduced, which leads to much smaller values for the refined nonbonded coefficients of the S atoms (Table 3). The bonding energy of the S...H interaction, W_{HB} , for each type of hydrogen bond was estimated as a function of the distance $r_{S...H}$ according to the Lippincott–Schroeder semiempirical function (Lippincott & Schroeder, 1955),

$$W_{HB} = -D_0^* \exp[-n^*(r_{S...H} - r_0^*)^2 / 2r_{S...H}] \times \exp[-(\theta/180)^2], \quad (7)$$

in which n^* is related to the S...H force constant k_0^* by the expression $n^* = k_0^* r_0^* / D_0^*$, r_0^* being the equilibrium distance of the SH bond. The empirical constant n^* and the values of D_0^* , k_0^* and r_0^* (Snyder, Schreiber & Spencer, 1973) are listed in Table 4.

The stretching of the N–H bond was neglected because of the weakness of the N–H...S bonding, while the interaction between N and S was treated as a Lennard–Jones potential. The last term in the equation represents the angular dependence (Hagler, Huler & Lifson, 1974), where θ is the supplement of the N–H...S angle. Since this effect turned out to be minor (ranging from a factor of 0.871 to 0.997 for the ferroelectric phase), we assumed the angular dependence in the modulated phase to be the same as in the ferroelectric phase, ignoring the effect of the modulation on the angles. For the calculation of the average phase the angular dependence of the paraelectric phase was used. The resulting energies are given in Table 5.

The reliability of the model parameters (Table 3) was tested by relaxing the structure. A set of ‘ideal’ cell

Table 4. Constants used in the Lippincott–Schroeder function

The constants are from Snyder, Schreiber & Spencer (1973); 1 mdyn = 10⁻¹⁸ J, 1 kcal mol⁻¹ = 4.1868 kJ mol⁻¹.

n^*	12.6 Å ⁻¹	k_0^*	4.14 mdyn Å ⁻¹
r_0^*	1.334 Å	D_0^*	63.2 kcal mol ⁻¹

Table 5. Hydrogen-bond lengths and calculated energies and force constants

Type	$r_{S...H}$ (Å)	θ (°)	W_{HB} (kcal mol ⁻¹)	Force constant (mdyn Å ⁻¹)	
				Calc.	Exp.*
Paraelectric phase					
A, B	2.397	11.1	-3.23	0.118	0.138
C, D	2.767	46.3	-0.55	0.017	0.060
E, F	3.055	56.5	-0.13	0.004	0.032
Average phase					
A, B	2.387		-3.37		
C, D	2.737		-0.64		
E, F	2.954		-0.21		
Modulated phase					
A	2.348–2.423		-3.37		
B	2.343–2.428		-3.34		
C	2.554–2.981		-0.71		
D	2.606–2.883		-0.69		
E	2.667–3.228		-0.33		
F	2.753–3.185		-0.26		
Ferroelectric phase					
A	2.354	10.5	-3.89	0.146	0.148
B	2.415	9.6	-2.99	0.108	0.129
C	3.038	64.8	-0.14	0.004	0.033
D	2.549	34.5	-1.57	0.054	0.096
E	2.669	44.7	-0.89	0.029	0.072
F	3.360	66.8	-0.03	0.001	0.017

* Bleckmann, Schrader, Meier & Takahashi (1971).

Table 6. Comparison of observed and energy-optimized results for the ferroelectric phase

Cell dimensions (Å)	Obs.	Minimal energy	
		Model A	Model B
a	7.516	7.214 (-0.302, 4.0%)*	7.803 (0.287, 3.8%)
b	8.519	8.020 (-0.499, 5.9%)	8.158 (-0.361, 4.2%)
c	5.494	5.601 (0.107, 1.9%)	5.656 (0.162, 2.9%)
Displacement from observed structure			
Molecule (I)			
R_y (°)	—	-0.138	-0.230
T_x (Å)	—	0.433	-0.046
T_z (Å)	—	0.185	0.084
Molecule (II)			
R_y (°)	—	-0.420	0.175
T_x (Å)	—	0.165	-0.063
W_{lat} (kcal mol ⁻¹)	-26.24	-27.38 (-1.14, 4.3%)*	-27.87 (0.72, 2.7%)
	-27.15		

* Difference between observed and energy-minimized values.

dimensions and molecular displacements was obtained with a modified Rosenbrock search procedure implemented in *WMIN*, in which a minimum lattice energy was reached (Table 6). The differences between the observed and ideal values are comparable with those achieved by Hagler & Lifson (1974).

It would be desirable to use experimental charge densities for the calculation of the Coulombic contribution. Such an approach has been discussed recently

Table 7. Energy (kcal mol⁻¹) comparison of different phases

The abbreviations are as follows: coul = Coulombic, disp = dispersive, rep = repulsive and lat = lattice energy.

Phases	W_{coul}	W_{disp}	W_{rep}	W_{lat}	
Model A					
Paraelectric	-12.13	-25.80	11.99	-25.95	
Average	-12.49	-27.31	13.38	-26.42	
Modulated ($\delta = 0.118$)	-12.56	-27.35	13.49	-26.42	
Ferroelectric	-12.68	-27.53	13.97	-26.24	
Model B					
Paraelectric	-12.13	-13.09	7.70	-7.82	-25.34
Average	-12.49	-13.89	8.64	-8.45	-26.19
Modulated ($\delta = 0.118$)	-12.56	-13.91	8.71	-8.70	-26.46
Ferroelectric	-12.68	-14.01	9.05	-9.51	-27.15

by Spackman, Weber & Craven (1988). Not only does it eliminate the dependence on the calculational method and basis set used, but it also incorporates any modification of the charge distribution due to the crystalline environment. We have used the κ -formalism (Coppens, Guru-Row, Leung, Stevens, Becker & Wang, 1979) to obtain a set of experimental atomic charges from previously collected X-ray data on thiourea (Kutoglu & Scheringer, 1982). The atomic charge of nitrogen [-0.94 (7)] was found to be rather unrealistically negative. Moreover, the so calculated Coulomb energy (about -4 kcal mol⁻¹) was much less negative than that obtained with the calculated charges (about -12 kcal mol⁻¹, Table 7). This suggests that an accurate data set for thiourea is still lacking, as also pointed out by Weber & Craven (1987).

Results and discussion

The lattice energies calculated with both models *A* and *B* are listed in Table 7 in order of decreasing temperature. The Coulomb and dispersion energy become more, and the repulsion energy less favorable as the temperature is lowered through successive phase

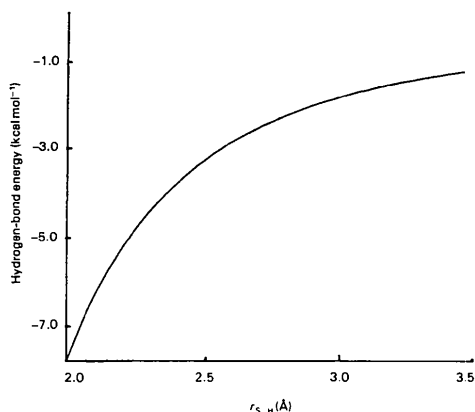


Fig. 2. The hydrogen-bond energy as a function of $r_{\text{S}\cdots\text{H}}$, as calculated with the parameters of Table 4. 1 kcal mol⁻¹ = 4.1868 kJ mol⁻¹.

transitions. The models successfully predict the total lattice energy of the ferroelectric phase to be lower than the energy of the high-temperature paraelectric phase, as required by thermodynamic considerations. This result was not achieved in a previous study (Dove & Lynden-Bell, 1986). For model *A*, the modulation distortion destabilizes relative to the average structure. This is reminiscent of the modulation occurring at the metal-insulator (Peierls) transition in low-dimensional organic salts such as TTF-TCNQ, which is electronically driven, but opposed by the elastic forces in the crystal. The lack of driving force in the non-hydrogen-bonding model *A* suggests that the specific introduction of hydrogen-bonding interactions (model *B*) is essential.

Since the Lippincott-Schroeder potential is strongly dependent on S...H distance, it can overcome the destabilizing effect of the other interactions on the modulation. In particular its negative curvature (Fig. 2) leads to a stabilization of symmetrical displacements from an average position. As evident from the numbers in Table 5 this stabilization is largest for the weaker hydrogen bonds, which are strengthened more by being shortened than they are weakened by being lengthened. Model *B* predicts the modulated phase to be intermediate in energy to the high- and low-temperature phases (Table 7), as required thermodynamically.

It is possible to estimate the hydrogen-bond force constants from the expression $k = W_{\text{HB}}/r_{\text{S}\cdots\text{H}}^2$. The resulting values (Table 5) are in good agreement with spectroscopic force constants given in the literature (Bleckmann, Schrader, Meier & Takahashi, 1971), thus providing further support for the model. Part of the differences may be attributed to Coulombic contributions which are relatively more important for the weaker, bent hydrogen bonds.

Conclusions

The calculational method for the lattice energy of modulated structures developed here is quite general. It can be applied to substitutionally modulated structures, and is easily extended to two-dimensional modulations.

In the present study the results indicate that the driving force for the modulation is to be sought in the extensive hydrogen-bonding network in thiourea. Since entropy effects are not included in the present treatment we cannot predict stability ranges; such a prediction can only be made on the basis of the Gibbs free energy. However, the calculations show that, at least in the case of thiourea, the thermodynamic condition that the low-temperature phases have the lower energy, can be accounted for by lattice-energy calculations.

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Absolute Crystal Structure of $C_9H_{12}O_4$ Determined by Three-Beam Scattering

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Abstract

(1*R*,5*S*)-8-Methoxy-3,3-dimethyl-2,4-dioxabicyclo-[3.3.0]oct-7-en-6-one, $C_9H_{12}O_4$, $M_r = 184.19$, orthorhombic, $P2_12_12_1$, $a = 18.296$ (2), $b = 7.8292$ (7), $c = 6.5741$ (7) Å, $V = 941.70$ Å³, $Z = 4$, $D_x = 1.299$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.958$ cm⁻¹, $F(000) = 392$, room temperature, final $R(F) = 0.064$ for 999 reflections. The absolute structure was determined by measurements of intensity changes in three-beam positions caused by multiple-scattering effects. A definite result was obtained in spite

of the poor quality of the crystal; the title compound has a (1*R*,5*S*) rather than a (1*S*,5*R*) configuration as originally proposed.

Introduction

According to Bestmann & Moenius (1986) the title compound has a (1*S*,5*R*) absolute configuration. Additional chemical investigations, however, gave rise to doubts with respect to this correlation. As the title compound is the basis for the synthesis of a series of